



---

*Institute of Paper Science and Technology*  
*Atlanta, Georgia*

---

**IPST TECHNICAL PAPER SERIES**



**NUMBER 413**

**ELECTRON TRANSFER REACTIONS IN PULPING  
SYSTEMS (VI): ALCOHOL BISULFITE PULPING**

**K. KURODA AND D.R. DIMMEL**

**JANUARY 1992**

# Electron Transfer Reactions in Pulping Systems (VI): Alcohol Bisulfite Pulping

K. Kuroda and D.R. Dimmel

Submitted to  
J. Wood Chem. Technol.

Copyright© 1992 by The Institute of Paper Science and Technology

For Members Only

## NOTICE & DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

# ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VI): ALCOHOL BISULFITE PULPING

Ken-ichi Kuroda\* and Donald R. Dimmel\*\*  
Institute of Paper Science and Technology  
575 14th Street, N. W.  
Atlanta, GA 30318

## ABSTRACT

Compound 1, which incorporates a hex-5-enyl group on a quinone methide precursor, has been used to demonstrate that  $\text{NaHSO}_3$  in 50% isopropyl alcohol exhibits electron transfer reactions. There is a significant solvent effect associated with this system since  $\text{NaHSO}_3$  in aq.  $\text{NaOH}$  showed very few products typical of an electron transfer system, while 50% isopropyl alcohol by itself at  $150^\circ\text{C}$  provided some of the typical products. The electron transfer ability of the 50% isopropyl alcohol/ $\text{NaHSO}_3$  system increases with increasing temperature but is less than that of aqueous anthrahydroquinone at similar temperatures.

## INTRODUCTION

Previous studies in our laboratory have been directed at demonstrating the importance of electron transfer reaction mechanisms for certain pulping systems. One of these studies<sup>1</sup> employed 5,5-dimethyl-6-hydroxy-6-(3,5'-dimethoxy-4'-hydroxyphenyl)-1-hexene, commonly referred by us as the "electron transfer detector" (ETD) compound. Under aqueous alkaline reactions conditions, anthrahydroquinone and

---

\*Visiting scientist at IPST 1990-91. Present address is The Institute of Agriculture & Forest Engineering, The University of Tsukuba, Tsukuba-shi, Ibaraki 305, Japan.

\*\*Please address correspondences to this author at IPST.

glucose showed the ability to transfer electrons, while sodium sulfide and sodium sulfite (the principal reagents in kraft and sulfite pulping processes) did not transfer electrons to ETD.

The reactions of ETD (1) are outlined in Scheme 1. At high temperature ETD is transformed to a quinone methide (2), a key intermediate in pulping reactions.<sup>2</sup> Electron transfer to 2 leads to the quinone methide radical anion  $2^{\cdot-}$ . Reduction of the radical anion directly or after cyclization produces 5 and 7-9. The ratio of cyclic (7-9) to acyclic (5) products formed depends on the relative rates of hydrogen atom transfer by the radical intermediates; a medium which readily supplies hydrogen atoms will give a larger amount of acyclic product, since intermediate  $2^{\cdot-}$  will be reduced before cyclization can occur. The occurrence of five-membered cyclic compounds in the product mixture is evidence that the quinone methide radical anion  $2^{\cdot-}$  had formed, and electron transfer reactions had occurred.

Sakai and co-workers have been examining the chemistry of alcohol bisulfite pulping.<sup>3-5</sup> They have suggested that the 50% alcohol sodium bisulfite system may be reacting by an electron transfer mechanism or a homolysis reaction mechanism.<sup>5</sup> We decided to examine these reaction conditions with the ETD compound and look for the production of five-membered ring cyclic products. The goal of this research was to verify whether the alcohol bisulfite cooking process involves single electron transfer reactions.

## RESULTS AND DISCUSSION

Table 1 lists the results of the reactions of ETD compound with  $\text{NaHSO}_3$  in 1 M NaOH in water and in 50% isopropyl alcohol (IPA), along with comparisons to reactions in 1 M NaOH, glucose and  $\text{Na}_2\text{SO}_3$  in 1 M NaOH, and 50% isopropyl alcohol. Glucose is an electron transfer reagent which shows a large amount of cyclized products. The product ratios are somewhat dependent on reaction temperature; there-



Table 1. Product Distributions<sup>a</sup> for the Reactions<sup>b</sup> of ETD (1)

product <sup>c</sup>	glucose 135°C 150°C		NaHSO <sub>3</sub> in IPA <sup>d</sup>		Na <sub>2</sub> SO <sub>3</sub>		NaHSO <sub>3</sub>		IPA <sup>d</sup>		1 M NaOH	
	135°C	150°C	135°C	150°C <sup>e</sup>	135°C	150°C	135°C	150°C	135°C	150°C	135°C	150°C
syringol	5.2	6.5	0.2		8.1	15.9	9.3	18.8	1.0	10.8	10.4	
syringaldehyde					11.0			13.4			39.3	
7	10.3	5.8	1.2	0.8	2.9		0.4			1.8		
8	7.5	5.1	0.7	0.5	2.6		2.6		0.2	1.8		
5a	52.0	46.2	10.9	46.5	6.0	0.4			30.8	6.0	0.2	
5b	2.8	9.7	3.9	7.1					0.8			
3	1.8	4.9	8.1	9.6								
unknown <sup>f</sup>			4.9	2.9					18.0	19.2		
9	5.2	16.0	3.6	13.7					13.0			
1 (ETD)	12.2	0.2	43.9	1.6	77.5	66.7	84.5	65.2	78.6	13.8	79.6	43.4
others	2.9	5.6	22.6	17.1	2.9	6.0	3.2	2.6	3.4	21.2		6.6

<sup>a</sup>Yields are based on relative integrated signal areas, expressed as a %, for those gas chromatography signals between 3-20 min retention time. <sup>b</sup>Unless noted differently the solvent was 1 M aqueous NaOH. The 150°C reaction time was 24 hr; the 135°C reaction time was 18 hr. <sup>c</sup>Listed in order of GC elution time. <sup>d</sup>Isopropyl alcohol, 50% with water, no added NaOH. <sup>e</sup>Reaction time of 21 hr. <sup>f</sup>GC/MS apparent mol. ion of 262.

fore, two temperatures were examined, 135°C (where much of our earlier results<sup>1</sup> were obtained) and 150°C. The structural assignments were based on comparing GC/MS results to the known mixture from the glucose reaction and available compounds.

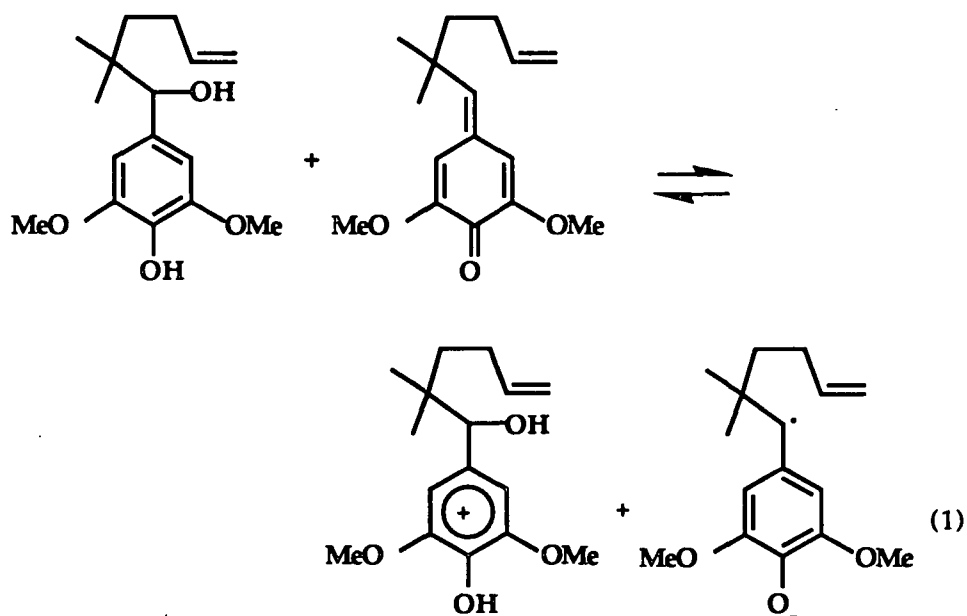
There are several interesting results indicated by the data in Table 1. First and foremost is that NaHSO<sub>3</sub> in IPA gives rise to both cyclic and acyclic reduction products, indicating that electron transfer reactions are occurring under these conditions. In fact, NaHSO<sub>3</sub>/IPA generates products similar in type and amounts to glucose in water at 150°C. The ability of the NaHSO<sub>3</sub> in IPA system to provide hydrogen atoms to reduce the radical intermediates appears to be greater than glucose. This conclusion stems from the higher levels of the first radical intermediate reduction product (3) and lower levels of the slower formed reduction products, 7 and 8, in the NaHSO<sub>3</sub>/IPA case.

Second, it is obvious from the results in the table that IPA plays a major role in promoting electron transfer reactions in the NaHSO<sub>3</sub> case. The small amount of electron transfer reactions observed with NaHSO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub> in water can be attributed to NaOH-induced reactions. This result confirms our earlier findings that sodium sulfite in 1 M NaOH has no ability to electron transfer.<sup>1</sup>

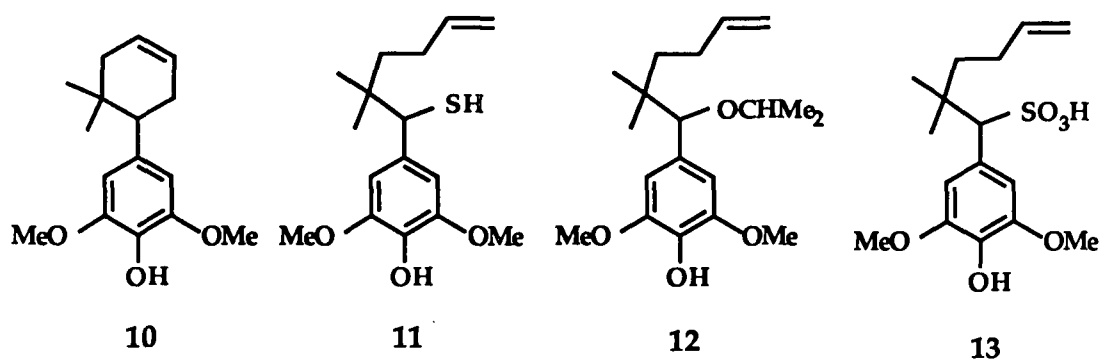
Isopropyl alcohol appears to have some ability to promote electron transfer reaction on its own. Both 5a and 9 were observed during heating ETD in IPA at 150°C; however, no reduction products are formed at 135°C. The electron transfer reactions may be a result of a process like that shown in eq. 1; however, we have no direct proof for the reactions shown.

Based on the observed GC/MS molecular weight (m/e 262) and fragmentation pattern, we suspect that the major (fast eluting) unknown produced in the IPA reactions is 10 or an isomer. Two slower eluting unknowns (classified as "others" in the table) have mass spectra





suggesting structures 11 and 12 as likely candidates. It is also probable that the  $\alpha$ -sulfonate 13 is a product but goes undetected because of its poor GC volatility.



Third, the rates of disappearance of the starting material are somewhat slow; ETD is generally still present in substantial amounts after 18 hr at 135°C in all the cases examined. The reagents and conditions listed in the table are not nearly as good in transferring electrons as anthrahydroquinone, which completely consumes ETD in 2 hr at 135°C in 1 M NaOH.

A follow-up experiment was performed to examine the time versus ETD amount with alcohol bisulfite treatment done at 160°C with a 2.7/1  $\text{NaHSO}_3$ /ETD ratio. This temperature and ratio were used to match that employed by Sakai and co-workers in their studies.<sup>5</sup> The ratio used previously (Table 1) was 8.5/1. Disappearance of ETD was followed by GC, using syringyl alcohol as an internal standard.

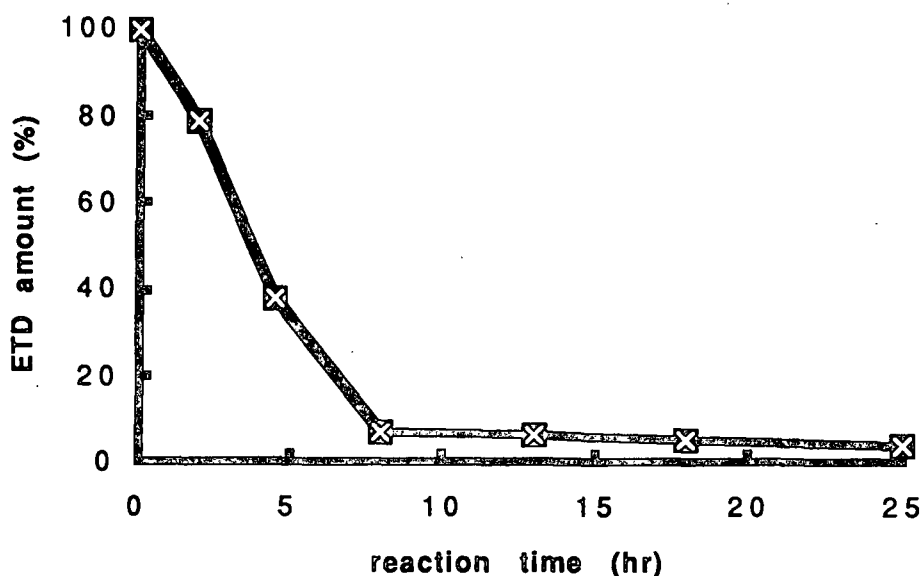


Fig. 1. Time decrease of ETD during alcohol bisulfite cooking at 160°C

About 93% of ETD was lost within the first 8 hr, after which the amount leveled to about 4%. The lack of complete reaction may have been due to the low level of  $\text{NaHSO}_3$  used. The yields of products 5a, 5b, 3 and 9 in the 2, 4.5, and 13 hr samples were also determined (Fig. 2). The GC response factor for syringyl alcohol to ETD was applied to estimate the yields of the products because authentic samples were not available.

The product distribution was somewhat different than the previous  $\text{NaHSO}_3$ /50% isopropyl alcohol treatment (Table 1); there was less relative amount of 5a/b products. This may be due to the lower level of  $\text{NaHSO}_3$  employed and/or changes in the relative rates of hydrogen

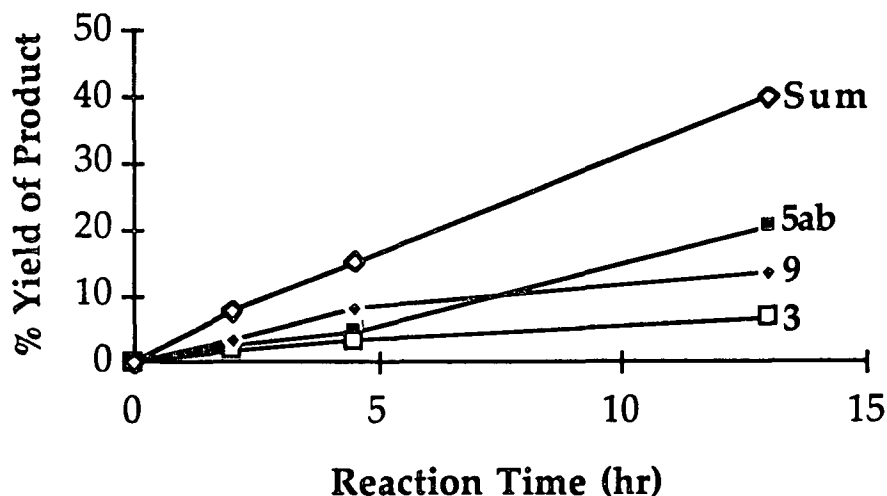


Fig. 2. Product yields with ETD and NaHSO<sub>3</sub> in 50% IPA at 160°C

atom abstraction and donation with a higher temperature. The progressive development of products suggests that once formed the products are relatively stable.

The total yield of products was about 40%. Considering the small amount of starting material remaining, we estimate that about 50% of the ETD was converted to products not detectable under the selected GC conditions. This trend was also observed when comparing GC intensities of the alcohol bisulfite treatments with the other treatments listed in Table 1. [It is not, however, apparent from the presentation of the data in Table 1, since the various GC areas were normalized.] The material unaccounted for may reflect the formation of involatile compounds, such as  $\alpha$ -sulfonate (13).

### CONCLUSIONS

The products observed upon heating compound 1 with NaHSO<sub>3</sub> in 50% isopropyl alcohol provide evidence that electron transfer reactions have occurred. It is obvious that the electron transfer reactions are being

aided by the solvent since  $\text{NaHSO}_3$  in aq.  $\text{NaOH}$  showed very few products typical of an electron transfer system, while 50% isopropyl alcohol at  $150^\circ\text{C}$ , in the absence of  $\text{NaHSO}_3$ , provided some of the typical products. The electron transfer ability of the 50% isopropyl alcohol/ $\text{NaHSO}_3$  system increases with increasing temperature, but is less than that of aqueous anthrahydroquinone at similar temperatures.

## EXPERIMENTAL

### *Materials*

Oxygen-free water was prepared by boiling distilled water for 30 min, bubbling nitrogen in the water as it cooled, and sealing the container until needed. Oxygen-free 1 M  $\text{NaOH}$  solution was prepared in a similar manner, using  $\text{O}_2$ -free water for dilution to the right molarity. Commercial  $\text{NaHSO}_3$  (J. T. Baker Chemical Co.),  $\text{Na}_2\text{SO}_3$  (Mallinckrodt, Inc.), glucose (Matheson Coleman and Bell Manufacturing Chemists),  $\text{NaOH}$  (Mallinckrodt, Inc.), and isopropyl alcohol (Aldrich Chemical Company, Inc.) were used without specific purifications.

### *Reactions of ETD*

All reactions of ETD were conducted in a nitrogen atmosphere with oxygen-free water in 4 mL stainless steel pressure vessels (bombs). Typically, each bomb contained 20 mg ( $70\ \mu\text{M}$ ) of ETD and 3.5 mL of solvent. The additives used for comparative study were as follows: glucose (113 mg, 13 mol. equiv. at  $150^\circ\text{C}$  and 63.1 mg, 5 mol. equiv. at  $135^\circ\text{C}^1$ ),  $\text{Na}_2\text{SO}_3$  (45.1 mg, 4.5 mol. equiv. at  $150^\circ\text{C}$  and 43.6 mg, 4.9 mol. equiv. at  $135^\circ\text{C}$ ),  $\text{NaHSO}_3$  (62.8 mg, 8.5 mol. equiv. at  $150^\circ\text{C}$  and 66.0 mg, 8.6 mol. equiv. at  $135^\circ\text{C}$ ), and 50% isopropyl alcohol.

The sealed bombs were rotated for selected time periods in a hot oil bath and then cooled quickly. The contents of bombs were neutralized with diluted  $\text{HCl}$ , if necessary, and extracted with chloroform. The

CHCl<sub>3</sub> solution was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub> overnight), and concentrated *in vacuo* below 40°C before analysis by the GC.

The reactions for estimating ETD and products as a function of time were carried out similarly; 20 mg (190 μM) of NaHSO<sub>3</sub> and 2 mL of 50% isopropyl alcohol were employed. The work-up was as described above except for the addition of known amounts of syringyl alcohol as an internal standard prior to the chloroform extraction.

### Analysis

The ETD reaction mixtures were analyzed by gas chromatograph (Hewlett-Packard HP 5890 GC) using a HP-17 packed column, helium carrier gas (flow rate 22.5 mL/min), and a temperature program of 150°C (2 min), 150 to 275°C at 5°C/min, and then held at 275°C. The injection port and the flame ionization detector (FID) were kept at 250°C and 275°C, respectively. For quantitative work, a known amount of syringyl alcohol was added as an internal standard prior to analysis. Identification of the GC signals was carried out by comparison with the published mass spectral fragmentation data<sup>1</sup> except for the following tentative assignments:

Compound 10 (six-membered ring side chain):

EI mass spectrum: *m/e* 262 (80%, M<sup>+</sup>), 180 (100%, ArCH=CH<sub>2</sub>), 167 (97%, ArCH<sub>2</sub><sup>+</sup>).

Isobutane CI mass spectrum: *m/e* 263 (100%, M + H<sup>+</sup>).

Compound 11 (α-sulfide):

EI mass spectrum: *m/e* 296 (100%, M<sup>+</sup>), 199 (98%, ArCHSH<sup>+</sup>).

Compound 12 (α-isopropoxy):

EI mass spectrum: *m/e* 322 (8%, M<sup>+</sup>), 280 (6%, M<sup>+</sup> - CH<sub>2</sub>=CHCH<sub>3</sub>), 167 (100%, ArCH<sub>2</sub><sup>+</sup>).

## REFERENCES

1. Smith, D. A. and Dimmel, D. R., J. Organic Chemistry, 1988, 53, 5428.
2. Gierer, J., Holzforschung, 1982, 36, 43.
3. Sakai, K., Mun, S.-P., and Imamura, H., J. Wood Chem. Technol., 1986, 6, 523.
4. Sakai, K., Takeuti, H., Mun, S.-P., and Imamura, H., J. Wood Chem. Technol., 1988, 8, 29.
5. Sakai, K., Takagi, T., and Imamura, H., J. Japan Wood Res. Soc., 1990, 36, 553.